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APPENDICES

Appendix A Preparation Of Piperazine Solution

From M = (g/Mw) × (1000/V)
Mw = molecular weight of piperazine (86.14 g/mol), V = volume of solvent (5 mL)
Piperazine was loaded into the activated carbon and silica gel adsorbent by adding the activated carbon and silica gel into the piperazine solution for 2 hours stirring at 500 rpm.

Table A1 Preparation of piperazine solution for the activated carbon

PZ weight (g)	Activated carbon weight (g)	wt %	Molar (M)
0.0231	1.0016	2.2543	0.0536
0.0540	1.0002	5.1224	0.1254
0.1014	1.0017	9.1923	0.2354
0.2030	1.0015	16.8535	0.4713

Table A2 Preparation of piperazine solution for the silica gel

PZ weight (g)	Silica gel weight (g)	wt %	Molar (M)
0.0216	1.0007	2.1129	0.0502
0.0523	1.0023	4.9592	0.1214
0.1016	1.0003	9.2204	0.2359
0.2035	1.0032	16.8642	0.4725

Appendix B Piperazine Calibration Curve

Preparation of 0.35 M piperazine stock solution required
Piperazine 3.0152 g in 100 mL ethanol solution
Preparation of piperazine concentration for calibration curve

$C_1V_1 = C_2V_2$

C_1 = the concentration of piperazine
V_1 = volume needed to prepare (10 mL),
C_2 = concentration of stock solution (0.3500 M)
V_2 = volume required to pipette

Table B1 The preparation of piperazine concentration for the calibration curve

$C_1 x10^{-3}$ (M)	V_1 (mL)	C_2 (M)	V_2 (mL)
1.0	10	0.3500	0.0286
5.0	10	0.3500	0.1429
10.0	10	0.3500	0.2857
15.0	10	0.3500	0.4286
20.0	10	0.3500	0.5714
25.0	10	0.3500	0.7143
30.0	10	0.3500	0.8571
50.0	10	0.3500	1.4286
70.0	10	0.3500	2.0000
90.0	10	0.3500	2.5714

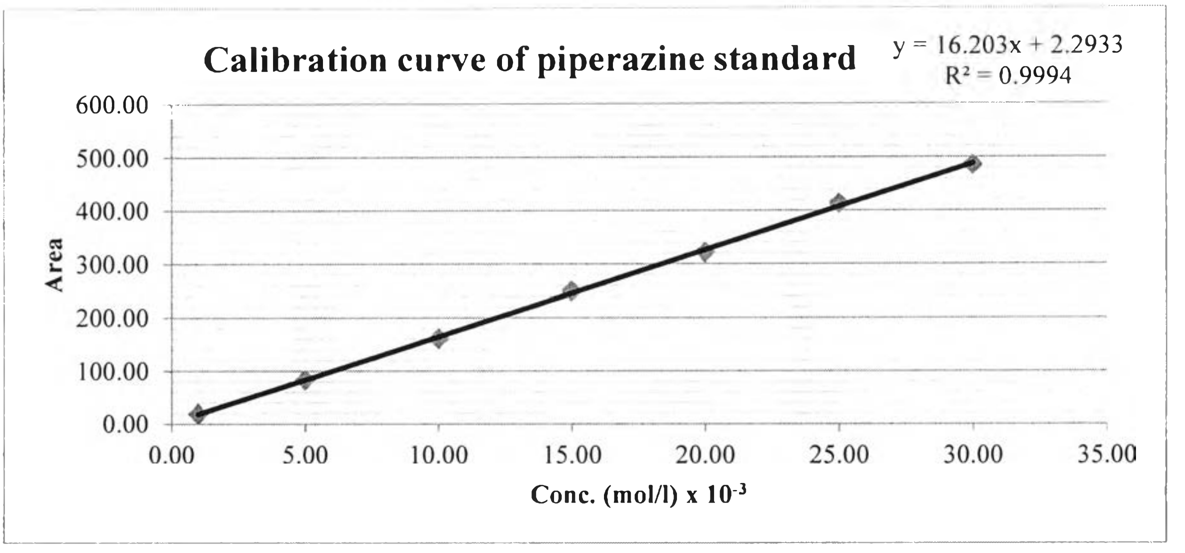

Figure B1 The calibration curve of piperazine standard

Analysis of Piperazine by GC-FID

After oven dry of the impregnated adsorbent, activated carbon was grinded. The activated carbon or silica gel adsorbent was weighted to dissolve the piperazine in 10 mL ethanol and in the final ethanol solution of 10 mL. Next, 10 injections of samples were injected into the GC-FID to find the unknown concentration of piperazine using the calibration curve from the equation y = 16.203x + 2.2933; where

y = peak area of piperazine,
16.203 = sensitivity,
2.2933 = interception,
and x = unknown piperazine concentration.

The weight of piperazine loading was calculated from M = (g/Mw) * (1000/V)

M = unknown piperazine concentration
= x (obtained from the calibration curve equation)
Mw = molecular weight of piperazine (86.14 g/mol)
V = volume of solvent (10 mL)
g = weight of piperazine loading

Weight of Adsorbent = Total weight – weight of piperazine

$$\text{Piperazine loading (wt \%)} = \frac{Weight\ of\ piperazine}{Weight\ of\ adsorbent+piperazine} * 100$$

Table B2 Samples of impregnated activated carbon; 10 wt % piperazine loading on activated carbon

	Sample weight (g)	Peak area	PZ (g)	PZ loading (wt %)
AC-PZ 10 wt%	0.6012	392.07 ±2.89	0.02072 ±0.00015	3.4467 ±0.0255
AC-PZ 10 wt%	0.2517	165.71 ±2.59	0.00869 ±0.00014	3.4515 ±0.0546
		Actual PZ loading (wt %)		3.4491

Table B3 Samples of impregnated silica gel; 30 wt % piperazine loading on silica gel

	Sample weight (g)	Peak area	PZ (g)	PZ loading (wt %)
SG-PZ 30 wt%	0.5000	783.99±10.23	0.04156 ±0.00054	8.3114 ±0.1087
SG-PZ 30 wt%	0.4202	661.43 ±9.61	0.03504 ±0.00051	8.3393 ±0.1215
		Actual PZ loading (wt %)		8.3254

PZ = 5 average piperazine injections ± SD,
Peak area = 5 average peak area ± SD,

Actual Piperazine loading (wt %) $\bar{x} = \frac{1}{2}(x_1 + x_2)$

$\bar{x}$ = actual piperazine loading,
x_1 = average piperazine loading of sample1,
x_2 = average piperazine loading of sample2

Appendix C Specification of Adsorbent and Equipment

Table C1 Specification of palm shell activated carbon

TECHNICAL SPECIFICATION	
Product	Granular activated palm shell based carbon
Grade	PH5 12 X 40 P
Test Method	ASTM, Unless otherwise stated
Application	Water purification, deodorization, decolourization, dechlorination and removal of organic compound in water
PHYSICAL PROPERTIES	SPECIFICATION
Apparent density (g/cc)	min. 0.48
Moisture (%w/w) (as packed)	max. 8
Ash (%w/w) (as packed)	max. 5
pH	9-11
Surface area (m^2/g)	min. 1150

Mass flow controller specifications:

- Model: GFC 17
- Flow range: 0 – 100 %
- Accuracy: ±1.5 %
- Repeatability: ±0.25 %
- Maximum Gas Pressure: 1000 psig
- Brand: AALBORG

Rotameter specifications:

- Model: PMR1-010266
- Accuracy: ±2 % FULL-SCALE
- Repeatability: ±0.25 %
- Maximum Pressure: 200 psig
- Brand: Cole-Parmer

Back pressure regulator specifications:

- Model: GH30XTHAXXXG
- Sensitivity: 0.05 PSI (0.345 kPa)
- Ambient Temperature Range: -20°F to +150°F (-29°C to +66°C)
- Maximum Pressure: 125 psig
- Brand: Conoflow

Appendix D Preparation for Standard Carbon Dioxide Concentration

Table D1 Actual flow (mL/min) of carbon dioxide and nitrogen from mass flow controllers by bubble flowmeter

Flow of CO_2 (mL/min)	**Actual Flow (mL/min)**			**Average Actual Flow (mL/min)**
	Trial 1	**Trial 2**	**Trial 3**	
5	13.5	13.6	13.5	13.5
10	21.3	21.6	21.4	21.4
15	28.3	28.4	28.4	28.4
20	35.9	35.8	35.9	35.9
25	44.1	44.2	44.2	44.2
30	49.1	49.2	48.9	49.1
35	57.7	57.7	57.9	57.8
40	63.3	63.4	63.4	63.4
45	71.2	71.4	71.4	71.3
50	80.7	81.0	81.1	80.9
55	85.9	85.7	86.0	85.9
60	91.0	91.3	90.8	91.0
65	99.6	100	100	99.9
70	105	106	107	106.0
75	113	114	114	113.7
Flow of N_2 (mL/min)	**Actual Flow (mL/min)**			**Average Actual Flow (mL/min)**
	Trial 1	**Trial 2**	**Trial 3**	
75	122	121	122	121.7

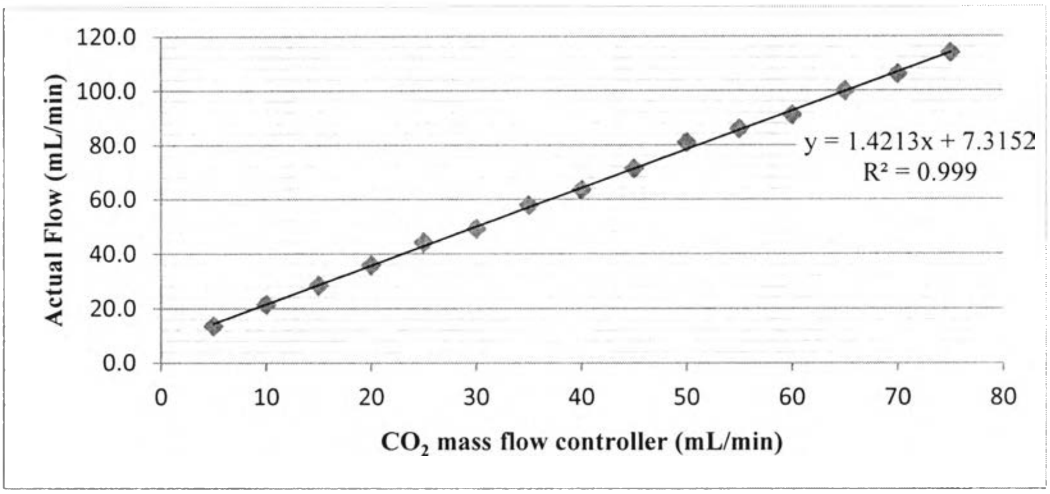

Figure D1 Calibration curve of standard CO_2 concentration by bubble flowmeter.

Preparation for CO_2 adsorption at 15% CO_2 concentration and adsorbent

After line cleaning-up, 1 g of adsorbent was filled into a tubular flow stainless steel adsorber column. The feed gas containing 15% CO_2 with a flow rate of 15 mL/min was allowed to flow into the packed bed adsorber to carry out the experiment at atmospheric pressure (14.7 psi), 30 psi, 50 psi, and 70 psi at room temperature until the CO_2 concentrations of feed gas at the outlet of adsorber reaches equilibrium.

Table D2 Adsorption data from Gas Chromatogram of pure activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	76.73	1.25	9.2840635	0.618940066
9	114.84	1.15	13.8952412	0.926353150
12	120.37	1.23	14.5643520	0.970960716
15	120.71	1.15	14.6054908	0.973703315
18	121.20	1.23	14.6647791	0.977655885
21	121.49	1.13	14.6998681	0.979995160
24	121.46	1.23	14.6962382	0.979753166

Table D2 (cont.) Adsorption data from Gas Chromatogram of pure activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
27	121.71	1.15	14.7264874	0.981769783
30	121.49	1.23	14.6998681	0.979995160
33	121.98	1.13	14.7591564	0.983947729
36	122.50	1.25	14.8220746	0.988142293
39	122.67	1.17	14.8426440	0.989513592
42	122.87	1.25	14.8668433	0.991126886
45	123.97	1.15	14.9999395	1

Retention Time = time that carbon dioxide appear, C_0 = CO_2 concentrations of the influent, C_A = CO_2 concentration of effluent stream of the column

Table D3 Adsorption data from Gas Chromatogram of pure activated carbon at pressure 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	64.20	1.27	7.8273591	0.521823945
9	95.86	1.17	11.6873933	0.779159555
12	111.04	1.25	13.5381614	0.902544095
15	116.86	1.17	14.2477445	0.949849630
18	120.22	1.25	14.6574006	0.977160042
21	121.71	1.17	14.8390636	0.989270910
24	122.14	1.25	14.8914899	0.992765992
27	121.83	1.15	14.8536942	0.990246281
30	122.72	1.25	14.9622043	0.997480289
33	122.44	1.17	14.9280663	0.995204422

Table D3 (cont.) Adsorption data from Gas Chromatogram of pure activated carbon at pressure 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
36	122.68	1.25	14.9573275	0.997155165
39	122.59	1.15	14.9463546	0.996423637
42	123.03	1.25	15	1

Table D4 Adsorption data from Gas Chromatogram of pure activated carbon at pressure 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	13.71	1.28	1.6704641	0.111363821
12	54.02	1.17	6.5819453	0.438794574
15	121.56	1.25	14.8112047	0.987409634
18	121.83	1.15	14.8441022	0.989602794
21	122.40	1.25	14.9135526	0.994232800
24	122.44	1.17	14.9184263	0.994557713
27	123.01	1.25	14.9878767	0.999187718
30	123.11	1.15	15.0000609	1
33	123.03	1.25	14.9903135	0.999350175
36	122.61	1.15	14.9391396	0.995938592

Table D5 Adsorption data from Gas Chromatogram of pure activated carbon at pressure 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	38.39	1.28	4.7320867	0.315473745
12	70.25	1.15	8.6592626	0.577286548
15	88.69	1.25	10.9322420	0.728819130
18	101.16	1.15	12.4693382	0.831292629
21	107.57	1.25	13.2594574	0.883967458
24	112.83	1.13	13.9078235	0.927192045
27	115.93	1.25	14.2899405	0.952666612
30	117.80	1.13	14.5204433	0.968033528
33	119.23	1.25	14.6967101	0.979784699
36	120.15	1.13	14.8101125	0.987344893
39	120.57	1.25	14.8618832	0.990796286
42	120.99	1.13	14.9136539	0.994247678
45	121.15	1.25	14.9333761	0.995562495
48	121.19	1.13	14.9383066	0.995891199
51	121.69	1.25	14.9999384	1

Table D6 Adsorption data from Gas Chromatogram of pure silica gel at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	88.42	1.43	10.1028336	0.673522243
6	127.51	1.35	14.5692413	0.971282754
9	129.12	1.42	14.7531993	0.983546618
12	129.51	1.33	14.7977605	0.986517367

Table D6 (cont.) Adsorption data from Gas Chromatogram of pure silica gel at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
15	129.81	1.40	14.8320384	0.988802559
18	131.28	1.33	15	1
21	130.61	1.42	14.9234461	0.994896405

Table D7 Adsorption data from Gas Chromatogram of pure silica gel at pressure 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	66.10	1.37	7.5210213	0.501403322
9	105.45	1.43	11.9983615	0.799893803
12	121.31	1.33	13.8029515	0.920200258
15	126.28	1.42	14.3684504	0.957900326
18	128.15	1.33	14.5812236	0.972085261
21	129.27	1.43	14.7086600	0.980581051
24	130.35	1.33	14.8315451	0.988773420
27	130.92	1.42	14.8964011	0.993097171
30	131.83	1.33	14.9999431	1
33	131.25	1.42	14.9339493	0.995600394
36	131.76	1.33	14.9919783	0.999469013

Table D8 Adsorption data from Gas Chromatogram of pure silica gel at pressure 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00		0	0
3	0.00		0	0
6	0.00		0	0
9	90.76	1.40	10.5192397	0.701282646
12	110.41	1.32	12.7967084	0.853113893
15	121.66	1.38	14.1006027	0.940040179
18	124.83	1.32	14.4680111	0.964534075
21	127.47	1.40	14.7739917	0.984932777
24	127.85	1.32	14.8180343	0.987868954
27	128.56	1.38	14.9003245	0.993354968
30	128.30	1.30	14.8701901	0.991346005
33	128.61	1.38	14.9061196	0.993741307
36	129.09	1.32	14.9617524	0.997450162
39	129.42	1.38	15	1
42	129.33	1.30	14.9895689	0.999304590
45	129.23	1.38	14.9779787	0.998531912

Table D9 Adsorption data from Gas Chromatogram of pure silica gel at pressure 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	80.72	1.37	9.2867004	0.619113361
12	97.90	1.25	11.2632306	0.750882037
15	112.87	1.35	12.9855039	0.865700261
18	118.62	1.25	13.6470318	0.909802117

Table D9 (cont.) Adsorption data from Gas Chromatogram of pure silica gel at pressure 70 psi and room temperature

Time (min)	**Peak area of CO_2**	**Retention Time**	**C_A**	**C_A/C_0**
21	121.56	1.35	13.9852738	0.932351588
24	123.55	1.25	14.2142199	0.947614665
27	125.42	1.35	14.4293603	0.961957355
30	126.32	1.27	14.5329038	0.968860255
33	126.93	1.37	14.6030833	0.973538886
36	128.11	1.28	14.7388403	0.982589354
39	128.18	1.38	14.7468937	0.983126246
42	128.61	1.28	14.7963645	0.986424298
45	128.84	1.37	14.8228256	0.988188372
48	129.36	1.28	14.8826507	0.992176714
51	129.43	1.38	14.8907041	0.992713606
54	130.32	1.30	14.9930971	0.999539807
57	130.38	1.38	15	1
60	130.35	1.30	14.9965486	0.999769903
63	129.95	1.38	14.9505292	0.996701948
66	129.33	1.30	14.8791993	0.991946618

Adsorption-regeneration cycle

The column was first fed with 15% CO_2 at the constant pressure (e.g. atmospheric pressure, 30 psi, 50 psi and 70 psi). The flow rate was kept at 15 mL/min. After the CO_2 concentrations of feed gas at the outlet of adsorber reached equilibrium, the column pressure was released to the atmosphere, the adsorption bed was then continuously regenerated by purging with 113 mL/min pure nitrogen at atmospheric pressure and room temperature. When the chromatogram showed no sign of CO_2 response. Then CO_2 adsorption was repeated and compared with the previous adsorption.

Table D10 Adsorption data from Gas Chromatogram of 3.45 wt % piperazine-activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	42.60	1.48	4.9646299	0.330976614
9	118.70	1.37	13.8333702	0.922228265
12	123.49	1.45	14.3915998	0.959443711
15	124.29	1.38	14.4848322	0.965659234
18	124.64	1.45	14.5256215	0.968378525
21	124.83	1.37	14.5477642	0.969854712
24	124.96	1.45	14.5629145	0.970864735
27	126.08	1.37	14.6934399	0.979566467
30	126.37	1.47	14.7272367	0.981819594
33	126.53	1.35	14.7458832	0.983062699
36	127.02	1.45	14.8029881	0.986869707
39	127.10	1.35	14.8123114	0.987491259
42	127.41	1.45	14.8484389	0.989899775
45	128.07	1.35	14.9253557	0.995027581
48	128.35	1.45	14.9579871	0.997203015

Table D10 (cont.) Adsorption data from Gas Chromatogram of 3.45 wt % piperazine-activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
51	128.71	1.35	14.9999417	1
54	128.43	1.43	14.9673104	0.997824567
57	128.55	1.37	14.9812952	0.998756895

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated three consecutive test cycles.

Table D11 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 3.45 wt % piperazine-activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	52.91	1.47	6.4404221	0.429359734
9	116.80	1.40	14.2173749	0.947821148
12	119.26	1.47	14.5168162	0.967783819
15	119.56	1.40	14.5533334	0.970218291
18	118.20	1.47	14.3877886	0.959182017
21	119.88	1.42	14.5922851	0.972815061
24	123.01	1.47	14.9732816	0.998214721
27	123.15	1.40	14.9903229	0.999350808
30	123.23	1.45	15.0000609	1
33	123.05	1.40	14.9781505	0.998539317
36	123.28	1.47	15.0061471	1.000405745

Table D12 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 3.45 wt % piperazine-activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	75.26	1.47	9.4177418	0.627846834
9	113.15	1.35	14.1591481	0.943939267
12	114.62	1.48	14.3430981	0.956202553
15	116.05	1.48	14.5220427	0.968132143
18	117.43	1.45	14.6947305	0.979644615
21	117.90	1.33	14.7535445	0.983565529
24	119.02	1.47	14.8936969	0.992908985
27	119.87	1.33	15.0000626	1
30	118.37	1.47	14.8123584	0.987486444

Table D13 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 3.45 wt % piperazine-activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	95.49	1.33	11.5121704	0.767481112
9	120.25	1.45	14.4972091	0.966484488
12	121.07	1.33	14.5960674	0.973075068
15	121.53	1.45	14.6515245	0.976772223
18	122.07	1.33	14.7166263	0.981112361
21	122.34	1.45	14.7491772	0.983282431
24	122.53	1.32	14.7720834	0.984809516
27	122.59	1.45	14.7793169	0.985291754

Table D13 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 3 of 3.45 wt % piperazine-activated carbon at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
30	124.42	1.33	14.9999397	1

Table D14 Adsorption data from Gas Chromatogram of 3.45 wt % piperazine-activated carbon at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	50.03	1.25	6.1286490	0.408574929
12	75.79	1.28	9.2842355	0.618946509
15	98.77	1.25	12.0992736	0.806614945
18	107.10	1.28	13.1196942	0.874642711
21	115.19	1.23	14.1107150	0.940710494
24	117.34	1.28	14.3740889	0.958268681
27	118.60	1.23	14.5284383	0.968558595
30	119.60	1.28	14.6509377	0.976725194
33	120.45	1.25	14.7550623	0.983666803
36	120.90	1.28	14.8101871	0.987341772
39	121.42	1.23	14.8738868	0.991588403
42	122.45	1.28	15.0000613	1
45	121.40	1.25	14.8714368	0.991425071

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated for three consecutive test cycles at 30 psi.

Table D15 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 3.45 wt % piperazine-activated carbon at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	57.23	1.50	6.8692761	0.457949908
12	92.18	1.32	11.0642997	0.737617028
15	107.88	1.47	12.9487595	0.863247180
18	118.19	1.33	14.1862615	0.945746980
21	122.50	1.48	14.7035877	0.980235257
24	122.79	1.33	14.7383962	0.982555814
27	124.26	1.47	14.9148392	0.994318637
30	124.97	1.33	15.0000600	1

Table D16 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 3.45 wt % piperazine-activated carbon at 30 psi and room temperature

Time (min)	Peak area of CO_2	RetentionTime	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	65.96	1.27	7.9681082	0.531207216
12	83.31	1.30	10.0640251	0.670935008
15	114.12	1.15	13.7859386	0.919062576
18	118.37	1.28	14.2993477	0.953289845
21	119.98	1.13	14.4938391	0.966255939
24	120.98	1.28	14.6146412	0.974309415
27	121.70	1.15	14.7016188	0.980107917
30	123.09	1.30	14.8695337	0.991302247
33	124.17	1.15	15	1

Table D17 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 3.45 wt % piperazine-activated carbon at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	72.35	1.50	8.7000962	0.580006413
12	101.29	1.33	12.1801347	0.812008979
15	115.83	1.47	13.9285714	0.928571429
18	119.16	1.33	14.3290043	0.955266955
21	121.70	1.47	14.6344396	0.975629309
24	122.86	1.33	14.7739298	0.984928652
27	123.20	1.47	14.8148148	0.987654321
30	123.61	1.33	14.8641174	0.990941158
33	123.89	1.47	14.8977874	0.993185827
36	124.74	1.32	15	1

Table D18 Adsorption data from Gas Chromatogram of 3.45 wt % piperazine-activated carbon at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	76.33	1.18	9.3009370	0.620064988
15	91.57	1.28	11.1579563	0.743866775
18	104.94	1.18	12.7871130	0.852477661
21	111.17	1.28	13.5462488	0.903086921
24	114.83	1.15	13.9922259	0.932818847
27	117.38	1.27	14.3029476	0.953533713

Table D18 (cont.) Adsorption data from Gas Chromatogram of 3.45 wt % piperazine-activated carbon at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
30	120.88	1.17	14.7294284	0.981965882
33	122.69	1.28	14.9499799	0.996669375
36	123.10	1.18	14.9999391	1
39	122.59	1.28	14.9377947	0.995857027

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated for three consecutive test cycles at 50 psi.

Table D19 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 3.45 wt % piperazine-activated carbon at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	76.57	1.43	8.9464522	0.596432466
15	99.18	1.45	11.5882085	0.772550241
18	111.79	1.42	13.0615631	0.870774264
21	119.27	1.45	13.9355276	0.929038791
24	122.89	1.35	14.3584890	0.957236330
27	125.38	1.45	14.6494211	0.976631874
30	125.68	1.35	14.6844731	0.978968687
33	126.51	1.43	14.7814505	0.985433868
36	127.07	1.35	14.8468810	0.989795918
39	127.33	1.45	14.8772594	0.991821156
42	127.73	1.33	14.9239955	0.994936906
45	128.12	1.43	14.9695631	0.997974762

Table D19 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 1 of 3.45 wt % piperazine-activated carbon at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
48	128.38	1.35	14.9999416	1

Table D20 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 3.45 wt % piperazine-activated carbon at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	80.19	1.33	9.6847826	0.645652174
15	95.93	1.48	11.5857488	0.772383253
18	107.05	1.33	12.9287440	0.861916264
21	112.35	1.47	13.5688406	0.904589372
24	117.25	1.32	14.1606280	0.944041868
27	120.91	1.47	14.6026570	0.973510467
30	121.15	1.30	14.6316425	0.975442834
33	123.01	1.47	14.8562802	0.990418680
36	123.47	1.32	14.9118358	0.994122383
39	124.20	1.48	15	1

Table D21 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 3.45 wt % piperazine-activated carbon at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0

Table D21 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 3 of 3.45 wt % piperazine-activated carbon at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
9	0.00	-	0	0
12	80.45	1.48	9.5327812	0.635516233
15	99.53	1.42	11.7936322	0.786239039
18	109.30	1.47	12.9513111	0.863417331
21	117.86	1.42	13.9656133	0.931037207
24	121.51	1.47	14.3981136	0.959870448
27	122.31	1.43	14.4929082	0.966190062
30	123.22	1.47	14.6007370	0.973378624
33	124.10	1.42	14.7050111	0.980330200
36	125.16	1.45	14.8306139	0.988703689
39	126.59	1.40	15.0000593	1

Table D22 Adsorption data from Gas Chromatogram of 3.45 wt % piperazine-activated carbon at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	0.00	-	0	0
15	98.42	1.20	11.9055972	0.793709677
18	107.32	1.30	12.9822057	0.865483871
21	112.40	1.20	13.5967194	0.906451613
24	116.50	1.28	14.0926851	0.939516129
27	118.98	1.20	14.3926839	0.959516129
30	119.68	1.30	14.4773610	0.965161290

Table D22 (cont.) Adsorption data from Gas Chromatogram of 3.45 wt % piperazine-activated carbon at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
33	121.96	1.18	14.7531663	0.983548387
36	122.25	1.28	14.7882468	0.985887097
39	123.07	1.18	14.8874399	0.992500000
42	123.36	1.30	14.9225205	0.994838709
45	124.00	1.18	14.9999395	1
48	123.06	1.28	14.8862303	0.992419355

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated for three consecutive test cycles at 70 psi.

Table D23 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 3.45 wt % piperazine-activated carbon at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	74.99	1.50	8.9345073	0.595631454
15	88.01	1.50	10.4857446	0.699046863
18	99.01	1.35	11.7963137	0.786417792
21	107.88	1.48	12.8531090	0.856870532
24	115.02	1.48	13.7037875	0.913582208
27	118.51	1.33	14.1195954	0.941302621
30	120.91	1.47	14.4055378	0.960365369
33	123.98	1.47	14.7713057	0.984749802
36	125.46	1.33	14.9476368	0.996505163
39	125.72	1.22	14.9786139	0.998570294

Table D23 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 1 of 3.45 wt % piperazine-activated carbon at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
42	125.90	1.30	15.0000596	1
45	125.67	1.22	14.9726568	0.998173153

Table D24 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 3.45 wt % piperazine-activated carbon at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	66.30	1.20	7.9325197	0.528834649
15	90.99	1.30	10.8865757	0.725771716
18	103.11	1.18	12.3366834	0.822445561
21	111.93	1.28	13.3919598	0.892797320
24	116.26	1.17	13.9100263	0.927335088
27	118.03	1.27	14.1217995	0.941453298
30	120.12	1.18	14.3718593	0.958123953
33	122.64	1.28	14.6733668	0.978224456
36	123.62	1.17	14.7906198	0.986041318
39	124.57	1.27	14.9042833	0.993618888
42	125.37	1.18	15	1
45	124.84	1.28	14.9365877	0.995772513

Table D25 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 3.45 wt % piperazine-activated carbon at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	76.05	1.48	8.9547493	0.596985635
15	90.57	1.33	10.6644530	0.710966324
18	103.55	1.50	12.1928244	0.812858152
21	112.80	1.48	13.2819951	0.885469817
24	118.74	1.33	13.9814193	0.932098281
27	121.74	1.48	14.3346639	0.955648010
30	124.06	1.50	14.6078397	0.973859800
33	125.09	1.32	14.7291203	0.981945207
36	126.30	1.48	14.8715956	0.991443598
39	127.39	1.48	14.9999411	1
42	127.13	1.32	14.9693266	0.997959023

Table D26 Adsorption data from Gas Chromatogram of 8.33 wt % piperazine-silica gel at atmospheric pressure (14.7 psi) and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	113.82	1.28	14.5091591	0.967281380
12	113.90	1.17	14.5193570	0.967961248
15	117.67	1.28	14.9999363	1.000000000
18	114.15	1.17	14.5512257	0.970085833
21	117.19	1.27	14.9387485	0.995920796

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated three consecutive test cycles.

Table D27 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 8.33 wt % piperazine-silica gel at 14.7 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	113.68	1.27	14.3935173	0.959567823
12	115.80	1.17	14.6619397	0.977462649
15	118.47	1.27	15	1

Table D28 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 8.33 wt % piperazine-silica gel at 14.7 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	117.51	1.30	14.5158302	0.967718027
12	119.35	1.22	14.7431226	0.982870790
15	120.20	1.32	14.8481217	0.989870708
18	121.43	1.30	15.0000618	1
21	121.41	1.20	14.99759119	0.999835296

Table D29 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 8.33 wt % piperazine-silica gel at 14.7 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0

Table D29 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 3 of 8.33 wt % piperazine-silica gel at 14.7 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
9	120.57	1.45	14.4868853	0.965796219
12	124.35	1.35	14.9410648	0.996074976
15	124.52	1.45	14.9614909	0.997436719
18	124.84	1.33	14.9999399	1.000000000
21	124.76	1.47	14.9903277	0.999359180

Table D30 Adsorption data from Gas Chromatogram of 8.33 wt % piperazine-silica gel at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	27.21	1.32	3.3487994	0.223252379
12	56.66	1.20	6.9732810	0.464883492
15	94.35	1.28	11.6118789	0.774122087
18	107.56	1.17	13.2376651	0.882507384
21	116.90	1.28	14.3871611	0.959140138
24	117.48	1.18	14.4585431	0.963898917
27	121.88	1.28	15.0000615	1
30	120.73	1.17	14.8585283	0.990564489
33	121.53	1.27	14.9569862	0.997128323

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated for three consecutive test cycles at 30 psi.

Table D31 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 8.33 wt % piperazine-silica gel at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	28.58	1.52	3.3841308	0.225607831
12	67.38	1.37	7.9784022	0.531891380
15	101.33	1.47	11.9983896	0.799889486
18	116.33	1.35	13.7745255	0.918298074
21	120.14	1.48	14.2256640	0.948373856
24	122.92	1.35	14.5548412	0.970318914
27	124.00	1.47	14.6827229	0.978844332
30	125.10	1.33	14.8129729	0.987527629
33	126.68	1.47	15.0000592	1
36	124.20	1.35	14.7064047	0.980423114
39	125.57	1.47	14.8686252	0.991237765

Table D32 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 8.33 wt % piperazine-silica gel at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	30.48	1.32	3.7170732	0.247804878
12	70.44	1.18	8.5902439	0.572682927
15	101.04	1.28	12.3219512	0.821463415
18	112.72	1.18	13.7463415	0.916422764
21	116.30	1.28	14.1829268	0.945528455
24	120.10	1.17	14.6463415	0.976422764

Table D32 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 2 of 8.33 wt % piperazine-silica gel at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
27	121.21	1.27	14.7817073	0.985447154
30	121.77	1.17	14.8500000	0.990000000
33	123.00	1.28	15.0000000	1
36	121.41	1.17	14.8060976	0.987073171
39	122.94	1.27	14.9926829	0.999512195

Table D33 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 8.33 wt % piperazine-silica gel at 30 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	32.35	1.50	3.8250978	0.255005518
12	86.34	1.35	10.2089319	0.680592779
15	108.44	1.47	12.8220590	0.854800568
18	120.03	1.33	14.1924728	0.946161123
21	122.59	1.45	14.4951699	0.966340848
24	124.08	1.35	14.6713490	0.978086079
27	124.52	1.47	14.7233751	0.981554470
30	125.18	1.33	14.8014142	0.986757055
33	126.86	1.45	15.0000591	1
36	125.65	1.33	14.8569875	0.990461927
39	126.28	1.47	14.9314793	0.995428031

Table D34 Adsorption data from Gas Chromatogram of 8.33 wt % piperazine-silica gel at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	52.52	1.20	6.3460609	0.423070727
15	85.33	1.28	10.3105365	0.687369099
18	103.74	1.18	12.5350411	0.835669406
21	111.32	1.28	13.4509425	0.896729499
24	117.77	1.18	14.2303045	0.948686966
27	119.10	1.28	14.3910101	0.959400677
30	121.87	1.18	14.7257129	0.981714194
33	122.98	1.28	14.8598357	0.990655711
36	123.23	1.17	14.8900435	0.992669567
39	123.52	1.28	14.9250846	0.995005639
42	124.14	1.18	15	1

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated for three consecutive test cycles at 50 psi.

Table D35 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 8.33 wt % piperazine-silica gel at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	43.65	1.20	5.2930263	0.352869846
15	99.16	1.18	12.0242036	0.801616815

Table D35 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 1 of 8.33 wt % piperazine-silica gel at 50 psi and room temperature

18	109.97	1.30	13.3350310	0.889005659
21	115.60	1.17	14.0177283	0.934518998
24	118.23	1.27	14.3366437	0.955780113
27	119.88	1.17	14.5367238	0.969118836
30	120.99	1.27	14.6713231	0.978092158
33	121.62	1.18	14.7477173	0.983185125
36	122.93	1.28	14.9065687	0.993775263
39	123.70	1.18	14.9999394	1
42	123.19	1.28	14.9380965	0.995877122

Table D36 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 8.33 wt % piperazine-silica gel at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	71.26	1.50	8.3776158	0.558507720
15	96.24	1.35	11.3143663	0.754291089
18	109.81	1.47	12.9097108	0.860647386
21	118.77	1.33	13.9630849	0.930872325
24	121.87	1.45	14.3275335	0.955168900
27	123.25	1.33	14.4897719	0.965984795
30	124.76	1.47	14.6672937	0.977819578
33	126.50	1.33	14.8718552	0.991457011
36	127.59	1.45	15	1
39	125.59	1.35	14.7648719	0.984324790

Table D36 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 2 of 8.33 wt % piperazine-silica gel at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
42	126.07	1.47	14.8213026	0.988086841

Table D37 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 8.33 wt % piperazine-silica gel at 50 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	79.57	1.48	9.3884582	0.625894754
15	101.86	1.35	12.0184536	0.801227091
18	112.13	1.47	13.2302101	0.882010541
21	120.31	1.35	14.1953677	0.946354126
24	122.29	1.47	14.4289878	0.961928735
27	124.31	1.35	14.6673274	0.977817982
30	125.03	1.47	14.7522802	0.983481476
33	125.75	1.33	14.8372329	0.989144970
36	127.13	1.47	15.0000590	1.000000000
39	125.51	1.35	14.8089153	0.987257139
42	125.54	1.47	14.8124550	0.987493118

Table D38 Adsorption data from Gas Chromatogram of 8.33 wt % piperazine-silica gel at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0

Table D38 (cont.) Adsorption data from Gas Chromatogram of 8.33 wt % piperazine-silica gel at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
6	0.00	-	0	0
9	0.00	-	0	0
12	0.00	-	0	0
15	55.55	1.30	6.7540457	0.450271541
18	79.82	1.17	9.7049132	0.646996839
21	97.14	1.30	11.8107651	0.787387533
24	107.04	1.13	13.0144565	0.867633947
27	112.35	1.28	13.6600727	0.910675205
30	117.00	1.13	14.2254429	0.948366702
33	118.99	1.28	14.4673970	0.964497041
36	119.95	1.12	14.5841186	0.972278512
39	121.28	1.27	14.7458266	0.983059090
42	123.37	1.12	14.9999392	1
45	121.69	1.30	14.7956764	0.986382427

After purging pure N_2 gas at atmospheric pressure, the CO_2 regeneration was repeated for three consecutive test cycles at 70 psi.

Table D39 Regeneration data from Gas Chromatogram of regeneration cycle 1 of 8.33 wt % piperazine-silica gel at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	0.00	-	0	0
15	56.61	1.28	6.8768222	0.458454810

Table D39 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 1 of 8.33 wt % piperazine-silica gel at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
18	83.28	1.15	10.1166181	0.674441205
21	100.75	1.30	12.2388241	0.815921607
24	111.41	1.15	13.5337707	0.902251377
27	115.87	1.28	14.0755588	0.938370586
30	120.14	1.15	14.5942663	0.972951085
33	121.02	1.30	14.7011662	0.980077745
36	122.09	1.17	14.8311467	0.988743116
39	123.11	1.28	14.9550534	0.997003563
42	123.23	1.17	14.9696307	0.997975381
45	123.48	1.28	15	1
48	123.22	1.13	14.9684159	0.997894396

Table D40 Regeneration data from Gas Chromatogram of regeneration cycle 2 of 8.33 wt % piperazine-silica gel at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	0.00	-	0	0
15	78.54	1.48	9.3625949	0.624175475
18	92.42	1.35	11.0172017	0.734483032
21	101.93	1.47	12.1508696	0.810061193
24	109.63	1.32	13.0687711	0.871254867
27	113.91	1.47	13.5789812	0.905269014
30	118.28	1.33	14.0999201	0.939998410

Table D40 (cont.) Regeneration data from Gas Chromatogram of regeneration cycle 2 of 8.33 wt % piperazine-silica gel at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
33	121.23	1.47	14.4515837	0.963442740
36	121.99	1.33	14.5421817	0.969482635
39	124.07	1.45	14.7901343	0.986012874
42	125.83	1.33	14.9999404	1
45	125.10	1.45	14.9129186	0.994198522

Table D41 Regeneration data from Gas Chromatogram of regeneration cycle 3 of 8.33 wt % piperazine-silica gel at 70 psi and room temperature

Time (min)	Peak area of CO_2	Retention Time	C_A	C_A/C_0
0	0.00	-	0	0
3	0.00	-	0	0
6	0.00	-	0	0
9	0.00	-	0	0
12	0.00	-	0	0
15	83.76	1.47	9.8703747	0.658024982
18	96.79	1.35	11.4058449	0.760389661
21	106.26	1.47	12.5218006	0.834786708
24	111.85	1.33	13.1805326	0.878702176
27	117.79	1.47	13.8805091	0.925367272
30	120.92	1.35	14.2493519	0.949956792
33	122.81	1.47	14.4720716	0.964804776
36	125.06	1.33	14.7372142	0.982480949
39	125.33	1.47	14.7690313	0.984602090
42	125.86	1.35	14.8314872	0.988765810
45	127.29	1.47	15	1
48	127.03	1.33	14.9693613	0.997957420

Table D42 Summarized data obtained for CO_2 adsorption

Adsorbent Type	Weight (g)	Adsorption pressure (psi)	Flow rate (mL/min)	Molar flow rate (mol/min) x10^{-4}	t_{tot} (min)	t_{matlab} (min)	t_q (min)	C_0	Qads (mmol/g)	Qads (mg/g)
Pure AC	1.0024	14.7	15.0	6.13	45	38.5256	6.4744	0.15	0.5943	26.1485
	1.0025	30	15.0	12.52	42	34.7673	7.2327	0.15	1.3551	59.6257
	1.0015	50	15.0	20.87	30	18.0454	11.9546	0.15	3.7368	164.4184
	1.0050	70	15.0	29.22	51	37.8851	13.1149	0.15	5.7193	251.6479
Pure SG	1.0050	14.7	15.0	6.13	18	15.3110	2.689	0.15	0.2462	10.8324
	1.0070	30	14.8	12.36	30	22.8418	7.1582	0.15	1.3174	57.9653
	1.0020	50	15.0	20.87	39	29.7230	9.277	0.15	2.8984	127.5294
	1.0074	70	15.0	29.22	57	46.0637	10.9363	0.15	4.7579	209.3473
3.45wt% PZ-AC	1.0004	14.7	14.8	6.05	51	43.4650	7.535	0.15	0.6838	30.0872
	1.0012	30	15.0	12.52	42	30.0469	11.9531	0.15	2.2425	98.6690
	1.0005	50	14.8	20.59	36	22.4535	13.5465	0.15	4.1822	184.0147
	1.0005	70	15.0	29.22	45	29.6598	15.3402	0.15	6.7199	295.6738
8.33wt% PZ-SG	1.0015	14.7	14.8	6.05	15	7.3057	7.6943	0.15	0.6975	30.6895
	1.0023	30	14.8	12.36	27	14.3034	12.6966	0.15	2.3476	103.2960
	1.0002	50	14.8	20.59	42	27.6329	14.3671	0.15	4.4368	195.2202
	1.0012	70	14.8	28.83	42	24.0935	17.9065	0.15	7.7340	340.2976
Regeneration Cycle 1 of 3.45wt% PZ-AC	1.0004	14.7	14.8	6.05	30	23.2342	6.7658	0.15	0.6140	27.0158
	1.0012	30	15.0	12.52	30	19.3850	10.615	0.15	1.9914	87.6234
	1.0005	50	14.8	20.59	48	34.6248	13.3752	0.15	4.1293	181.6878
	1.0005	70	15.0	29.22	42	27.6991	14.3009	0.15	6.2646	275.6419
Regeneration Cycle 2 of 3.45wt% PZ-AC	1.0004	14.7	14.8	6.05	27	20.8567	6.1433	0.15	0.5575	24.5301
	1.0012	30	15.0	12.52	33	22.4594	10.5406	0.15	1.9775	87.0093
	1.0005	50	14.8	20.59	39	25.6862	13.3138	0.15	4.1103	180.8537
	1.0005	70	15.0	29.22	42	27.7639	14.2361	0.15	6.2362	274.3929
Regeneration Cycle 3 of 3.45wt% PZ-AC	1.0004	14.7	14.8	6.05	30	24.3549	5.6451	0.15	0.5123	22.5408
	1.0012	30	15.0	12.52	36	26.1246	9.8754	0.15	1.8527	81.5183
	1.0005	50	14.8	20.59	39	25.7540	13.246	0.15	4.0906	179.9867
	1.0005	70	15.0	29.22	39	25.0238	13.9762	0.15	6.1224	269.3834
Regeneration Cycle 1 of 8.33wt% PZ-SG	1.0015	14.7	14.8	6.05	15	7.3111	7.6889	0.15	0.6970	30.6680
	1.0023	30	14.8	12.36	33	20.5823	12.4177	0.15	2.2961	101.0269
	1.0002	50	14.8	20.59	39	25.0739	13.9261	0.15	4.3006	189.2279
	1.0012	70	14.8	28.83	45	27.6786	17.3214	0.15	7.4813	329.1783
Regeneration Cycle 2 of 8.33wt% PZ-SG	1.0015	14.7	14.8	6.05	18	10.3214	7.6786	0.15	0.6961	30.6269
	1.0023	30	14.8	12.36	33	20.8673	12.1327	0.15	2.2434	98.7082
	1.0002	50	14.8	20.59	36	22.4842	13.5158	0.15	4.1739	183.6527
	1.0012	70	14.8	28.83	42	24.9125	17.0875	0.15	7.3804	324.7366

Regeneration Cycle 3 of 8.33wt% PZ-SG	1.0015	14.7	14.8	6.05	18	10.3779	7.6221	0.15	0.6909	30.4015
	1.0023	30	14.8	12.36	33	21.4479	11.5521	0.15	2.1360	93.9846
	1.0002	50	14.8	20.59	36	23.0036	12.9964	0.15	4.0135	176.5951
	1.0012	70	14.8	28.83	45	28.2836	16.7164	0.15	7.3176	321.9740

Molar flow rate = $Molar\ flow\ rate = \frac{P \times V}{R \times T}$

Example

Calculation of pure activated carbon at atmospheric pressure (14.7 psi)

The parameters were

- P = Pressure = 1 atm = 101325 Pa
- V = Volume ($15\ m^3 \times 10^{-6}$)
- R = 8.31451 $Pa \times m^3 \times K^{-1} \times mol$
- T = Temperature (K) = 25 °C + 273 = 298 K

$$t_q = \int_0^{\infty} \left(1 - \frac{C_A}{C_0}\right) dt$$

t_q = stoichiometric time determined from the breakthrough curve via MATLAB software

$$Q_{ads} = \frac{F C_0 t_q}{W}$$

- Q_{ads} = dynamic adsorption capacity (0.5943 mmol/g)
- F = molar flow rate (6.13 mol/min)$\times 10^{-4}$
- C_0 = 0.15
- T_q = 6.4744 mins
- W = 1.0024 g

The summary of the normalized CO_2 adsorption capacity

of pure activated carbon at atmospheric pressure (14.7 psi)

$$\text{sorption capacity } (\mu mol/m^2 \cdot g) = \frac{CO_2 \text{ adsorption capacity (mmol/g)}}{\text{Total surface area } (m^2/g)} \times 1000$$

$$= \frac{0.5943}{925.4} \times 1000$$

$$= 0.6422$$

	Pure AC		Impregnated AC		Pure SG		Impregnated	
)	20-40		20-40		230-300		230-300	
ce area (m^2/g)	925.4		845.3		557.3		478.7	
surface area (m^2/g)	795.8		727		-		-	
urface area (m^2/g)	129.6		118.3		557.3		478.7	
volume (cc/g)	0.439		0.399		-		-	
olume (cc/g)	0.073		0.073		0.792		0.675	
re diameter (Å)	22.1		22.3		56.9		56.4	
adsorption	mmol/g	μmol/m^2·g	mmol/g	μmol/m^2·g	mmol/g	μmol/m^2·g	mmol/g	μm
14.7	0.5943	0.6422	0.6838	0.8089	0.2462	0.4418	0.6975	1
30	1.3551	1.4643	2.2425	2.6529	1.3174	2.3639	2.3476	4
50	3.7368	4.0380	4.1822	4.9476	2.8984	5.2008	4.4368	9
70	5.7193	6.1804	6.7199	7.9497	4.7579	8.5374	7.7340	1

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Presentation:

1. Praekiat, D., Saiwan, C., and Tontiwachwuthikul, P. (2014, May 7-8) Carbon Dioxide Adsorption Using Adsorbents Impregnated with Piperazine. Paper presented at International Conference on Environment and Renewable Energy, Paris, France.

Study of Improving Carbon Dioxide Adsorption Capacity Using Adsorbents Impregnated Piperazine

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ABSTRACT

The adsorption of carbon dioxide (CO_2) for the natural gas processing application was performed with adsorbents modified with piperazine (PZ). To optimize CO_2 adsorption capacity, the effects of adsorption pressure, PZ loading, and types of adsorbents (activated carbon, or AC, and silica gel, or SG) were studied. Piperazine was impregnated onto the surface of AC and SG adsorbents by the wet impregnation method. The surface morphology of the unimpregnated and impregnated adsorbents was characterized using a surface area analyzer. The PZ loading was detected by a gas chromatography-flame ionization detector. It was found that the maximum PZ loading on the AC and SG were 3.45 wt% and 8.33 wt%, respectively. In the CO_2 adsorption and regeneration experiments, the adsorbents were tested in a stainless steel reactor. The breakthrough curves obtained from the feed gas containing 15% CO_2/N_2 with a flow rate of 15 mL/min were determined by using a gas chromatography-thermal conductivity detector. The effects of adsorption pressure were carried out at 298 K at various pressures, i.e. 14.7, 30, 50, and 70 psi. The results showed that PZ impregnated on AC and SG at pressure 70 psi showed the highest CO_2 adsorption capacity of 6.7 mmol/g and 7.7 mmol/g, respectively. The efficiency of regeneration of the impregnated adsorbents was more than 85 % during three consecutive test cycles.

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INTRODUCTION

Carbon dioxide is the main component of greenhouse gases among other greenhouse gases due to its abundance, which is produced not only from burning fossil fuels, coal, oil, natural gases, but also from the industrial sources, such as chemicals and petrochemical manufacturing. Exploration of effective methods to stabilize the atmospheric concentration of CO_2 is an urgent task of the world. Surrounding by different strategies proposed for CO_2 mitigation, carbon capture and storage (CCS) is recognized as a major technology to reduce the global emission of anthropogenic CO_2. There are various CO_2 capture technologies, such as cryogenic techniques, membrane purification, liquid absorption phenomena in liquids and solid adsorption. Among these technologies, solid adsorption processes are suggested to be a promising way that it avoids equipment corrosion, large equipment size, high energy cost in regeneration problems encountered by chemical absorption. Previous work studied on the CO_2 adsorption using activated carbon modified with piperazine (Watana *et al.*, 2013). In this work, the adsorbent will be impregnated with piperazine to improve the adsorption capacity. In order to utilize the full surface of the adsorbent with maximum loading for maximum adsorption capacity, it is recommended to choose a wider pore adsorbent to reduce the pore blockage. This study chooses silica gel and activated carbon to be the adsorbents.

EXPERIMENTAL

A. Materials

In this study, two types of adsorbents were investigated; the commercial activated carbon which was granular activated palm shell based carbon supplied by CARBOKARN Co., Ltd., (Thailand). The other is the commercial silica gel, particle size 230-400 mesh, pore size 60 Å (technical grade) was purchased from Sigma-Aldrich. Piperazine anhydrous (PZ, AR grade, ≥ 99%) with a molecular weight of 86.14 g/mol was obtained from Merck. Ethanol (AR grade, 99 %) with a molecular weight of 46.07 g/mol was obtained from RCI Labscan, Thailand.

B. Experimental setup

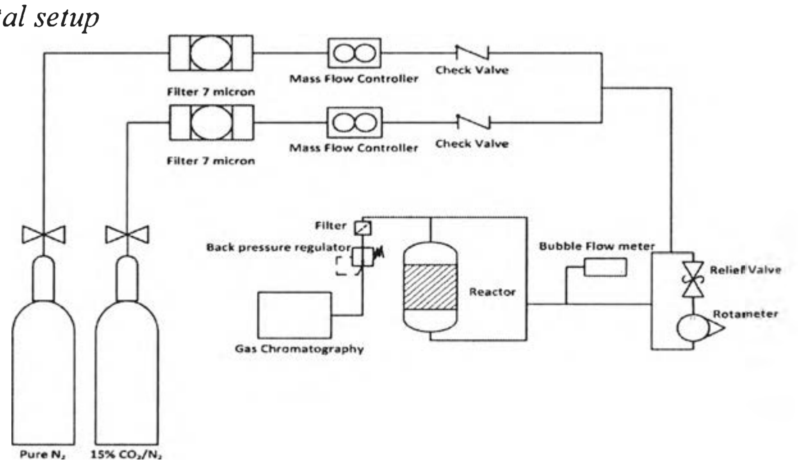

Figure 1: Schematic flow diagram for CO_2 adsorption.

In Figure 1, the outlet flow rate released from the gas cylinders is controlled by mass flow controllers for line of 15 % CO_2/N_2 and line of pure N_2. The 15% CO_2 passed through the rotameter which the flow rate is adjusted to 15 mL/min determined by a bubble flow meter. Before testing CO_2 adsorption in the adsorption column, the 15% CO_2 gas was analyzed by a gas chromatography-thermal conductivity detector (GC-TCD) in comparison with the calibration curve of CO_2 gas. The adsorption column was a tubular flow stainless steel adsorber with an inner cell diameter of 4 mm, outer cell diameter of 6 mm, and 31 cm long. It was vertically oriented for the even distribution of adsorbent. In the top and bottom 10 cm of the column, the adsorbent was packed and emplaced with glass wool to support the adsorbent and covered with glass bead at the top layer, and the feed was running against gravity. To maintain a constant pressure of CO_2 gas, back pressure regulator was used. A pressure gauge was used to monitor the column pressure. The concentrations of product stream were finally analyzed by a gas chromatograph.

C. Preparation of adsorbents

To obtain a dry cleaned and proper size activated carbon, a granular size activated carbon was ground by milling jar and sieved to acquire a 20-40 mesh size followed by heating in a 60 °C oven for 6 h and kept in the desiccators at room temperature to avoid the moisture effect. The constant mesh size was controlled throughout the experiments. For silica gel, it was used without further pretreatment.

D. Preparation of piperazine impregnation onto adsorbents

PZ in adsorbent was prepared by wet impregnation. The dry AC of 20-40 mesh size was impregnated by varying four different weight percent of PZ, 2 wt %, 5 wt %, 10 wt %, and 20 wt % to the total weight of adsorbent. For example, 2 wt %, 0.02 g of PZ crystals was dissolved in 5 mL of ethanol until finally dissolved then mixed with 1.0 g of AC. The mixtures were mixed in a 50 mL beaker at 500 rpm using a magnetic bar on a stirring hot plate (C-MAG HS10 IKA®, USA) for 2 h, after that it was filtered using a suction pump. The impregnated PZ then was filtered to dry in the oven at 60 °C for 1 ½ h to completely eliminate ethanol. The procedure was repeated for the preparation of the PZ impregnated SG with 5 wt %, 10 wt %, and 20 wt % i.e. 0.05 g, 0.10 g, and 0.20 g of PZ. The PZ-SG was prepared with the same way as the PZ-AC.

E. Characterization of adsorbents

The prepared adsorbents were characterized by various techniques described as follows.

- Surface area analysis

Surface area analyzer (Autosorb-1MP, Quantachrome, USA) was used to analyze the surface area of the adsorbent and identify the effects before and after PZ loading via the impregnation method.

- Degree of piperazine loading (wt %) on impregnated adsorbent

The impregnated AC was crushed into fine particles, and then the adsorbent was weighed and dissolved in 10 mL of ethanol. The solution was heated at 60 °C and stirred at 250 rpm for an hour to complete dissolution of PZ from the adsorbent. After 1 h, the solution was cooled to room temperature then the volume was made up to 10 mL with ethanol. The fine particle of adsorbent was filtered using filter paper No. 1. 0.04 μL of the filtrate was injected using a 1 μL syringe (SGC syringe) into the gas chromatography-flame ionization detector (GC-FID) via heated injection port at 200 °C with the split flow of 10 mL/min helium carrier gas. The DB® -5 column with 0.53 mm id x 1.0 μm film thickness x 30 m length was used to operate at an initial temperature of 50 °C, a ramp rate of 10 °C /min and isothermal temperature of 120 °C.

F. CO_2 adsorption-regeneration

In the CO_2 adsorption and regeneration experiments, adsorbent was tested in a stainless steel reactor. The conditions for each experiment performed were 15 mL/min of 15 % CO_2 feed gas flow at room temperature (25 °C). The effects of adsorption pressure were carried out at various pressures, i.e. 14.7, 30, 50, and 70 psi. To obtain the adsorption capacity and breakthrough curve for packed bed CO_2 adsorption, Rt®-Q-BOND column with 0.53 mm id x 20 μm film thickness x 30 m length was used to operate at an isothermal temperature of 40 °C. The GC-TCD injection port was heated to 100 °C with the spilt flow of 8 mL/min helium carrier gas. In typical CO_2 adsorption, after line cleaning-up, 1.0 g of adsorbent was filled into a tubular flow stainless steel adsorber column, while purging with N_2 gas at 113 mL/min. Then, 15% CO_2 of dry gas at 15 mL/min was allowed to flow into the packed bed adsorber to carry out the experiment at room temperature and atmospheric pressure until the CO_2 concentrations of feed gas at the outlet of the adsorber reached equilibrium. The concentrations of CO_2 in the downstream in terms of chromatogram were continuously monitored using computer and WiniLab III V4.6 program in the computer.

The dynamic adsorption capacity of the adsorbent (Q_{ads}) was calculated by Eq. (1),

$$Q_{ads} = \frac{FC_0 t_q}{W} \quad (1)$$

Where F (mol/min) is the total molar flow of feed gas, C_0 is the CO_2 concentration of the inlet stream, W is the mass of solid adsorbent loaded in the column, and t_q (min) is the stoichiometric time which was determined from the breakthrough curve according to Eq. (2) via MATLAB software version 7.10.0.499 (Guerreero *et al.*, 2010).

$$t_q = \int_0^{\infty} \left(1 - \frac{C_A}{C_0}\right) dt \quad (2)$$

Where C_0 and C_A are the CO_2 concentrations of inflow and outflow gas stream of the column.

To investigate the regenerability efficiency of the adsorbent, adsorption-regeneration cycle measurement were carried out. In this study, the column was first fed with 15% CO_2 at the constant pressure (e.g. atmospheric pressure, 30 psi, 50 psi and 70 psi). The flow rate was kept at 15 mL/min. After the CO_2 concentrations of feed gas at the outlet of adsorber reached equilibrium, the column pressure was released to the atmosphere, the adsorption bed was then continuously regenerated by purging with 113 mL/min pure nitrogen at atmospheric pressure and room temperature until the chromatogram showed no sign of CO_2 response during desorption. Then CO_2 adsorption was repeated and compared with the previous adsorption.

RESULTS AND DISCUSSION

A. Characterization Results

To understand the surface morphology, surface area analysis was applied in order to distinguish the changes of non-impregnated and impregnated adsorbent pore volume and pore size distribution.

- *Impregnated activated carbon*

Table 1: The surface area analysis of non-impregnated and impregnated activated carbon

Adsorbing Bed	Surface area (m^2/g)			Pore volume (cc/g) $x10^{-1}$			Average pore diameter(Å)
	Total	Mesopore	Micropore	Total	Mesopore	Micropore	
Non-impregnated activated carbon	925.4	901.5	881.6	5.12	3.08	4.39	22.14
10 wt % piperazine - activated carbon	845.3	864.9	803.3	4.72	2.99	3.99	22.35

There is a decrease in the surface area and pore volume of the micropore more than the change in the mesopore (Table 1). The decrease in the surface area could indicate that there was some amount of PZ blocking in the micropore which resulted in the decrease in pore volume. However, from the result it can be assumed that 10 wt % PZ was not totally loaded into the pore site of the AC because there was only a small decrease in the pore volume of the micropore and not even in the mesopore.

- *Impregnated silica gel*

There is a decrease in the surface area and pore volume of the non-impregnated and 30 wt % PZ-SG, the pore properties are listed in Table 2. The SG is a typical mesoporous material. The total surface area and total pore volume of 30 wt % PZ-SG decrease because of the increase of the loading amount of PZ.

Table 2: The surface area analysis of non-impregnated and impregnated silica gel

Adsorbing Bed	Total surface area, (m^2/g)	Mesopore surface area, (m^2/g)	Total pore volume, $(cc/g)x10^{-1}$	Mesopore volume, $(cc/g)x10^{-1}$	Average pore diameter(Å)
Non-impregnated silica gel	557.3	814.4	7.92	8.56	56.9
30 wt % piperazine -silica gel	478.7	715.2	6.75	7.33	56.4

The PZ loading was detected by a gas chromatography-flame ionization detector. A calibration curve was done to determine the concentration of an unknown sample in the adsorbent by comparing with PZ standards of known concentration. It was found that the maximum PZ loading on the AC and SG were 3.45 wt% and 8.33 wt%, respectively. Due to the pore site of adsorbent, it can assume that the mesoporous structure of SG that have high pore volume and high pore diameter channel structure

B. Effects of adsorption pressure and breakthrough curve results

Figure 2 shows the breakthrough curves of impregnated AC and impregnated SG at different pressure and room temperature. The monitor displayed 0 % of CO_2 molecules in the beginning of the experiment as the CO_2 molecules were being fully adsorbed by the surface and the pore sites. When CO_2 molecules start to breakthrough out from the adsorbent, CO_2 monitor would display values greater than 0% until the curve was entering its saturation stage as showing the S-shape and reaches C/C_0 =1 at the equilibrium stage.

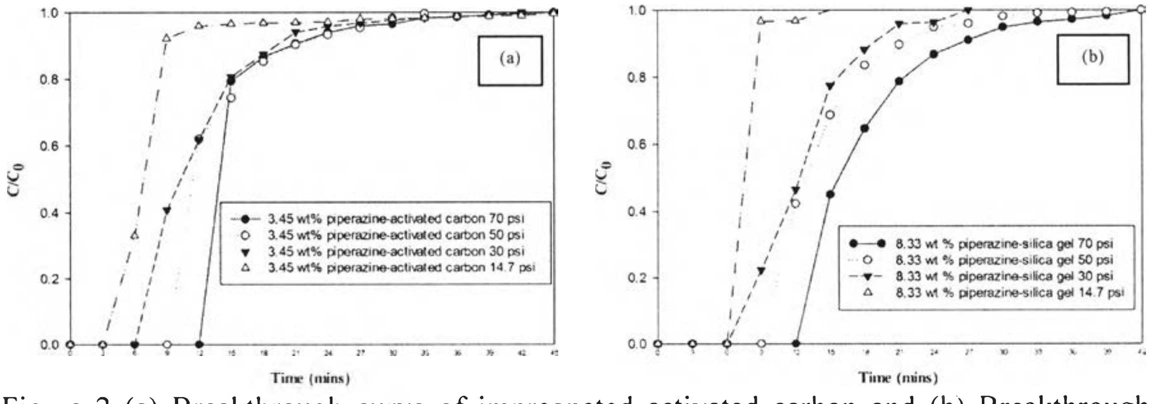

Figure 2 (a) Breakthrough curve of impregnated activated carbon and (b) Breakthrough curve of impregnated silica gel at 14.7 psi, 30 psi, 50 psi, and 70 psi.

From the result obtained, the adsorption capacities of unimpregnated adsorbents at 14.7 psi, 30 psi, 50 psi, and 70 psi were 0.5943, 1.3551, 3.7368, and 5.7193 mmol/g for pure AC and 0.2462, 1.3174, 2.8984, and 4.7579 mmol/g for pure SG, respectively. Comparing with the impregnated adsorbents, the adsorption capacities at 14.7 psi, 30 psi, 50 psi, and 70 psi were 0.6838, 2.2425, 4.1822, and 6.7199 mmol/g for 3.45 wt % PZ-AC and 0.6975, 2.3476, 4.4368, and 7.7340 mmol/g for 8.33 wt % PZ-SG, respectively. The unimpregnated adsorbent initial reached saturation stage because of the limited active sites available. The impregnated adsorbent would take longer time to reach of the saturation stage. Because the carbon dioxide molecules are attached to the available active sites by chemisorption between CO_2 and PZ molecules; therefore, at an elevating pressure, the attractive force between the surface of the adsorbent and the carbon dioxide molecules is increasing. It was observed that the CO_2 adsorption capacity of impregnated adsorbent increases with the enhanced of PZ. The breakthrough times of CO_2 increased with the increase in pressure. By comparing with PZ-AC, the PZ-SG results showed a rapid saturation stage. This indicated that the microporous of AC structures have the higher available active sites than mesoporous structure of SG. The CO_2 adsorption- regeneration cycles were shown in Figure 3. The efficiency of regeneration of the impregnated AC was more than 85 % and the efficiency of regeneration of the impregnated SG was more than 90 % during three consecutive test cycles.

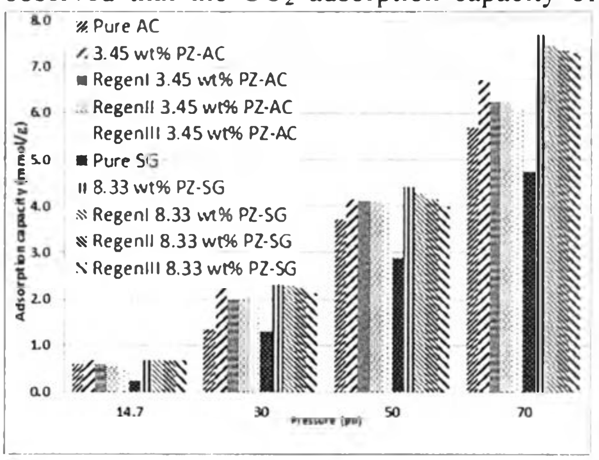

Figure 3 The CO_2 adsorption capacity (mmol/g) during three consecutive test cycles.

CONCLUSIONS

The adsorbents impregnated with PZ and the adsorption pressure strongly impact on CO_2 adsorption capacity of the prepared adsorbents. The PZ impregnated AC and impregnated SG at pressure 70 psi exhibited the highest CO_2 adsorption capacity of 6.7 mmol/g and 7.7 mmol/g, respectively. The efficiency of regeneration of the impregnated adsorbents was more than 85 % during three consecutive test cycles.

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